Selective Pyrolysis of Japanese Cedar to C_1-Chemistry Materials. II : Particle Size, Portion of Wood, Temperature and Time Dependence of CO Percentages in Produced Gases, and Kinetic Investigation

AUTHOR(S):

Nakagawa, Tetsuo; Minato, Kazuya; Katayama, Yukio

Selective Pyrolysis of Japanese Cedar to C_1-Chemistry Materials. II. Particle Size, Portion of Wood, Temperature and Time Dependence of CO Percentages in Produced Gases, and Kinetic Investigation

Tetsuo NAKAGAWA*, Kazuya MINATO** and Yukio KATAYAMA***

C_1 化学の原料としてのスギの選択的熱分解 II. 生成気体中の CO の占める割合の粒子サイズ，部位，温度，時間依存性ならびに速度論的解釈

中川徹夫*・湊 和也**・片山幸士***

Résumé

To obtain a detailed information on wood as raw materials for C_1-chemistry, the experimental results in our previous paper were analysed, and the kinetics of the reaction was discussed. In view of the carbon monoxide (CO) percentage in produced gases from pyrolyzed Japanese cedar (*Cryptomeria japonica* D. Don), its percentage was found to be higher as a pyrolysis temperature was higher. However, it was barely irrespective of the size and portion of wood collected, and pyrolysis time. The activation energies obtained experimentally were 8.73×10^4 J mol^{-1} and 9.07×10^4 J mol^{-1}, respectively, for sapwood and heartwood portions in the temperature range between 200 and 300°C. These values were in a good agreement in the order of magnitude with those in the references.

和文要旨

木材を C_1 化学の素原料として役立てるための詳細な情報を得るために，前報で得られたスギ熱分解実験結果を生成気体中の一酸化炭素（CO）の割合の観点から検討した。さらにこの反応の速度論についても考察した。すなわち，処理温度が高いほど，生成気体中の CO の割合は高くなり，試料の粒子のサイズ，試料の採取部位，分解時間にはほとんど無関係であった。また，

* 中川徹夫：京都府立山城高等学校定時制課程。
Part-time Course, Kyoto Prefectural Yamashiro Senior High School, 29 Sakata-cho, Taishogun, Kita-ku, Kyoto, 603.

** 湊 和也：京都大学農学部林産工学科。
Department of Wood Science and Technology, Faculty of Agriculture, Kyoto University, Sakyo-ku, Kyoto, 606-01.

*** 片山幸士：京都大学大学院農学研究科地域環境科学専攻。
Division of Science and Technology of Regional Environment, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto, 606-01.

200°Cから300°Cの温度範囲における反応の活性化エネルギーは，辺材の場合が8.73×10^4 J mol^{-1}，心材の場合が9.07×10^4 J mol^{-1}であり，文献値と同じオーダーであることが判明した。

1. INTRODUCTION

To obtain a basic information on wood as raw materials for C_1-chemistry, we have performed a pyrolysis of Japanese cedar (*Cryptomeria japonica* D. Don) powder in our previous paper[1], and discussed particle size, portion of wood (sapwood and heartwood), pyrolysis temperature and time against weight loss and the conversion ratio of the produced gas to carbon monoxide (CO). As a result, we found that the temperature was higher as the weight loss and the conversion ratio were greater. However, we have neither analyzed our results in view of the CO percentage in produced gases, nor referred to the kinetics of this reaction.

The purpose of this paper is, therefore, to obtain the additional information on wood as raw materials for C_1-chemistry on the size and portion of wood, pyrolysis temperature and time against CO percentage in produced gases through an analysis of our previous results[1]. Moreover, we have discussed the kinetics of the reaction by the use of the first-order reaction model, and obtained the frequency factor and activation energy of the rate constant.

2. EXPERIMENTAL

Experimental conditions have already given in the previous paper[1]. In brief, the pyrolyses were carried out using a Shimadzu pyrolyzer PYR-IA equipped with a Shimadzu gas chromatograph GC-7AG.

3. RESULTS AND DISCUSSION

3.1 CO percentages in produced gases

Temperature dependence

In order to discuss appropriate conditions about the conversion of wood powder to CO, we would like to propose the following two equations:

$$P=\frac{w_{CO}}{w_{CO_2}}, \tag{1}$$

$$Q=\frac{w_{CO}}{w_{CH_4}+w_{CO_2}}, \tag{2}$$

where w_i is the weight of the produced gas i (i = CO, CO_2, or CH_4). It is necessary to raise the P and Q values in order to utilize wood for C_1-chemistry material.

Figure 1 shows the relationship between the pyrolysis temperature and the P value. The pyrolysis period was ten minutes. The P value for sapwood is increased linearly in the temperature range between 200 and 600°C, but is increased greater over the temperature

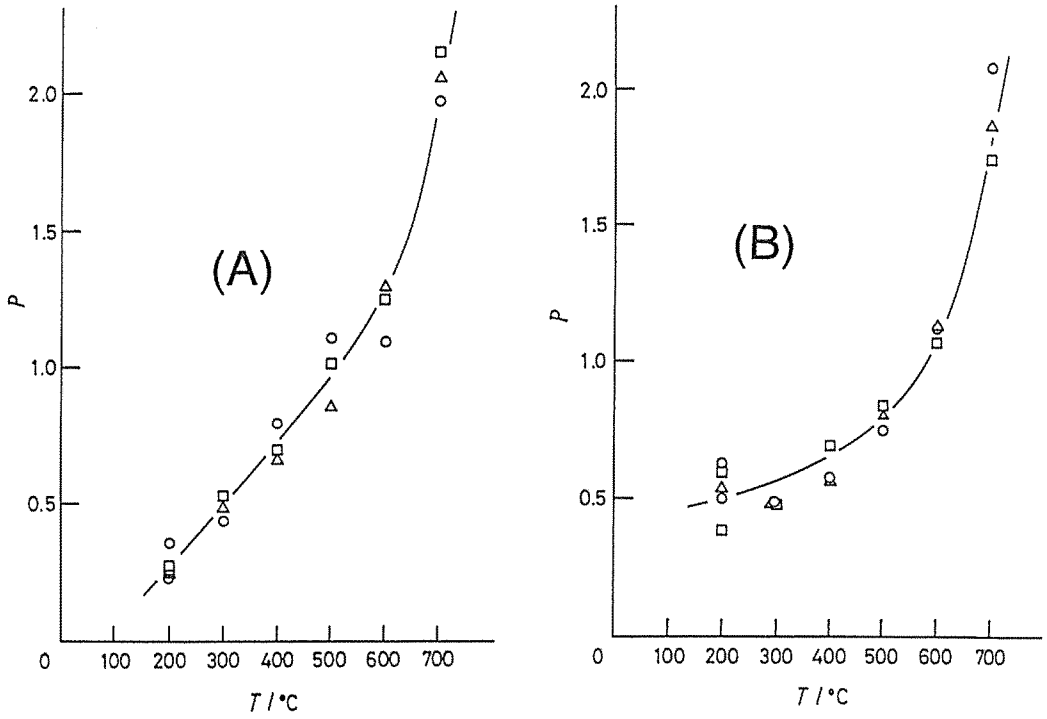

Fig. 1. Relationship between pyrolysis temperature (T) and weight ratio of CO to CO_2 (P). (A) and (B) represent sapwood and heartwood, respectively. Pyrolysis period is 10 minutes. ○, △, and □ are for 60-80, 80-100, and 100-150 mesh, respectively.

of 600°C. The similar pattern was observed for heartwood but the P value was more slowly increased below 600°C.

Figure 2 demonstrates the relationship between pyrolysis temperature and the Q value. The pyrolysis period was ten minutes. The pattern of the Q value in Fig. 2 resembles that of the P values in Fig. 1 for both sapwood and heartwood. The sudden enlargement of the Q value in the temperature range between 600 and 700°C implies the increase of CO gas produced. Comparing Fig. 1 with Fig. 2, we can admit that the CH_4 gas is also increased in its amount in the temperature range of 600 to 700°C range.

We may, therefore, conclude that the effective pyrolysis requires the higher temperature pyrolysis in view of the CO percentage in produced gases, and we can estimate the validity of our previous results.

Time dependence

Tables 1 and 2 indicate the relationship between the pyrolysis time and the P and Q values at 300°C and 700°C, respectively. It is obvious that the P and Q values are indifferent to pyrolysis times, particle size, and portion of wood collected.

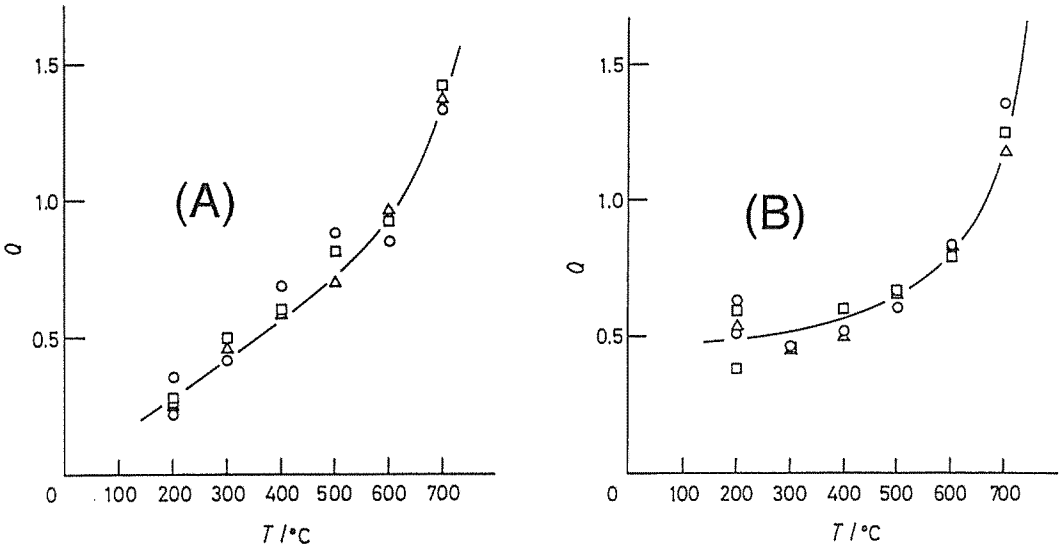

Fig. 2. Relationship between pyrolysis temperature (T) and weight ratio of CO to CH_4+CO_2. Pyrolysis period is 10 minutes. Legends are the same as in Fig. 1.

Table 1 Relationship between pyrolysis time and weight ratio of CO to other gaseous products at 300 °C

(a) sapwood

t/min		1	5	10	20
P	60-80 mesh	0.44	0.46	0.44	0.61
	100-150 mesh	0.43	0.48	0.53	0.54
Q	60-80 mesh	0.44	0.44	0.42	0.56
	100-150 mesh	0.43	0.43	0.49	0.50

(b) heartwood

t/min		1	5	10	20
P	60-80 mesh	0.55	0.47	0.49	0.52
	100-150 mesh	0.48	0.50	0.49	0.36
Q	60-80 mesh	0.55	0.45	0.46	0.50
	100-150mesh	0.47	0.47	0.47	0.35

3.2 Kinetics for this pyrolysis reaction

Apparent rate constant and apparent activation energy

It is of great interest to study a mechanism of the pyrolysis reaction with the aid of the kinetics. Because the kinetics of wood and cellulose has already been investigated[3~10], we can compare our results with these previous studies. Therefore, in this section, we focus on the kinetics of this reaction. Supposing that the first-order reaction is applied to this initial pyrolysis one[2], we can draw the following equation:

Table 2 Relationship between pyrolysis time and weight ratio of CO to other gaseous products at 700 °C

(a) sapwood

	t/min	1	5	10
P	60-80 mesh	1.99	1.78	1.97
	100-150 mesh	2.49	1.83	2.14
Q	60-80 mesh	1.38	1.17	1.33
	100-150 mesh	1.58	1.34	1.41

(b) heartwood

	t/min	1	5	10
P	60-80 mesh	1.59	1.58	2.07
	100-150 mesh	1.75	1.31	1.74
Q	60-80 mesh	1.09	1.08	1.35
	100-150 mesh	1.19	0.96	1.17

$$\frac{dW}{dt} = -kW, \qquad (3)$$

where W is the weight of wood meal, t the time, and k the apparent rate constant. Equation (3) is reduced to[2],

$$\ln\left(\frac{W}{W_i}\right) = -kt, \qquad (4)$$

where W_i is the initial weight of wood meal.

Figures 3 and 4 indicate the relationship between the pyrolysis time and the natural logarithm of weight loss of wood meal at 200 °C and 300°C, respectively. We

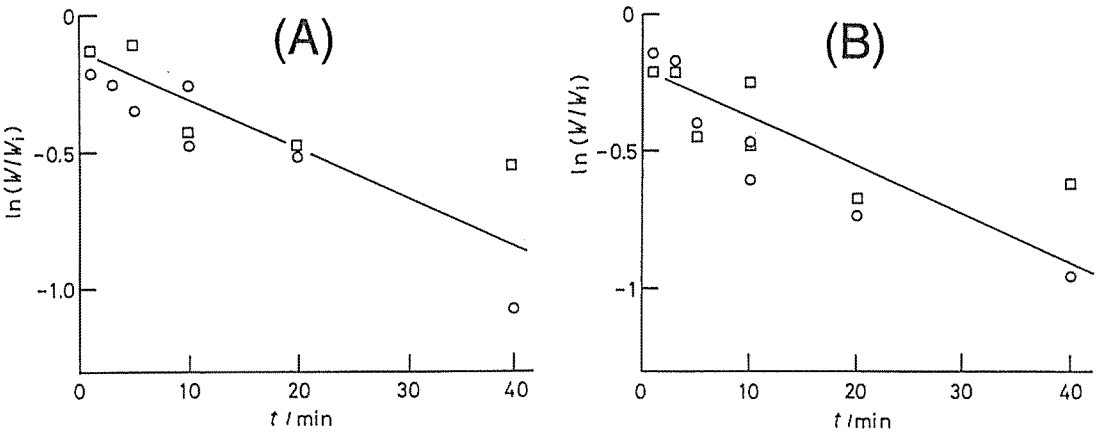

Fig. 3. Relationship between pyrolysis time (t) and natural logarithm of weight loss of Japanese cedar wood meal. Pyrolysis temperature is 200°C. Legends are the same as in Fig. 1.

obtained the apparent rate constants k by using initial linear parts, and summarized them in Table 3.

In general, the rate constant k is represented as[2,3],

$$k = A \exp\left(\frac{-E_a}{RT}\right), \qquad (5)$$

or

$$\ln k = \ln A - \frac{E_a}{RT}, \qquad (6)$$

where A is the frequency factor, E_a the activation energy, R the gas constant, and T the absolute temperature.

Figure 5 shows the relationship between the reciprocal absolute temperature and the

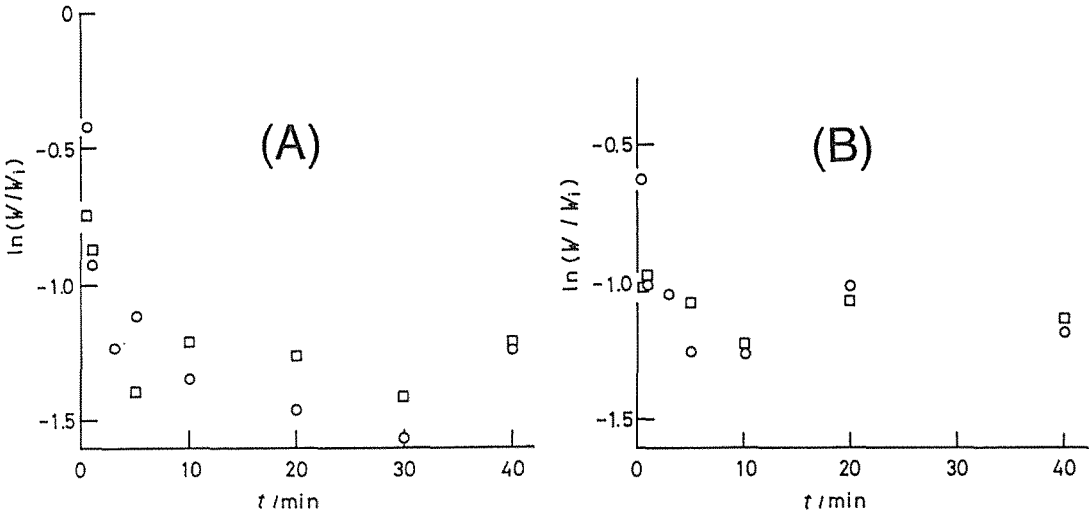

Fig. 4. Relationship between pyrolysis time (t) and natural logarithm of weight loss of Japanese cedar wood meal. Pyrolysis temperature is 300°C. Legends are the same as in Fig. 1.

Table 3 Relationship between temperature (T) and the rate constant (k).

(a) sapwood

T/K	473	573	673	773	973
k/min^{-1}	0.0178	0.900	1.35	1.66	2.03

(b) heartwood

T/K	473	573	673	773	973
k/min^{-1}	0.0177	0.994	1.39	1.55	2.00

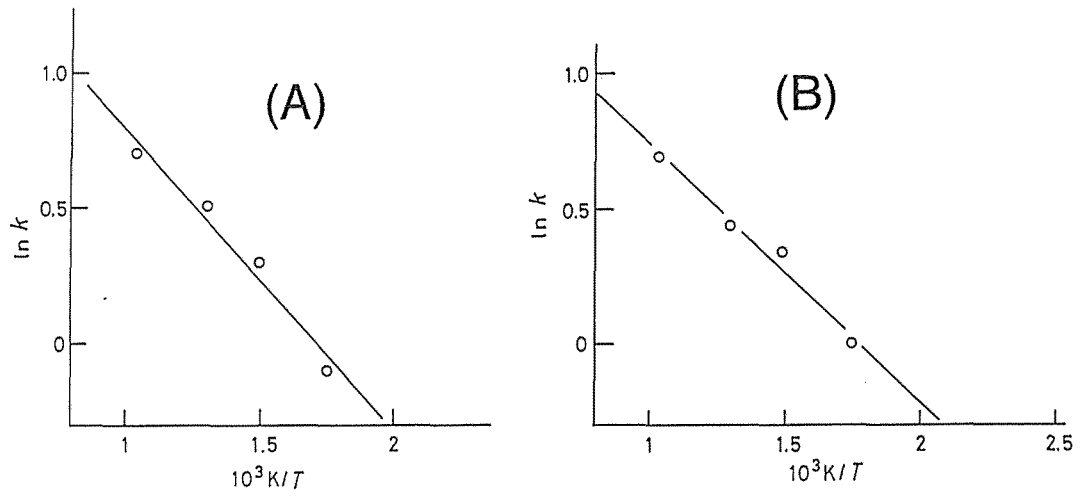

Fig. 5. Relationship between reciprocal pyrolysis temperature ($1/T$) and natural logarithm of rate constant at temparature range between 300 and 700°C. (A) and (B) represent sapwood and heartwood, respectively.

Table 4 Frequency factor (A) and activation energy (E_a)

(a) Present work

	Sapwood		Heartwood	
	300~700°C	200~300°C	300~700°C	200~300°C
A /min^{-1}	6.83	7.80×10^{7}	5.41	1.87×10^{8}
E_a /J mol^{-1}	9.40×10^{3}	8.73×10^{4}	7.92×10^{3}	9.07×10^{4}

(b) References

	Sitka spruce wood meal [3]	Douglas fir wood meal [3]	White pine wood meal [5]
	200~275°C	110~220°C	245~325°C
A /min^{-1}	4.08×10^{11}	3.18×10^{7}	9.00×10^{9}
E_a /J mol^{-1}	1.40×10^{5}	1.04×10^{5}	1.15×10^{5}

natural logarithm of the rate constant, namely, Arrhenius plot for this pyrolysis reaction. The data at 200°C are eliminated because of the large deviation of the first order regression lines. From the lines, we obtained the frequency factors and the activation energies of this reaction shown in Table 4. However, the frequency factor and the activation energies in this work are smaller than those in references[3,5]. These facts imply that the main pyrolysis reaction does not occur in the temperature range between 300 and 700°C. Therefore, we tried to recalculate them by using the data at 200°C and 300°C. The new results obtained are also listed in Table 4, and these values are of the same order of magnitude as in the references. The difference between experimental values and references is probably due to the experimental conditions such as a sort of wood species, size, atmosphere, pyrolysis time, and so on. These findings suggest that the main dissociating reaction occurs in the temperature range of 200 to 300°C.

Moreover, we cannot admit the difference between the activation energy of sapwood and that of heartwood. Probably the pyrolyzing mechanism for sapwood is the same as that for heartwood.

4. Conclusions

We have performed the pyrolysis of Japanese cedar (*Cryptomeria japonica* D. Don) wood meal, and discussed the particle size and portion of wood (sapwood and heartwood) collected, pyrolysis temperature and time against CO percentage in produced gases, and discussed the kinetics of this reaction.

The rate constants of the main pyrolysis reaction are $7.80\times10^{7}\exp(8.73\times10^{4}\ \mathrm{J\ mol^{-1}}/RT)\ \mathrm{min^{-1}}$ and $1.87\times10^{8}\exp(9.07\times10^{4}\ \mathrm{J\ mol^{-1}}/RT)\ \mathrm{min^{-1}}$ for sapwood and heartwood, respectively. The frequency factors and activation energies for sapwood resemble those for heartwood, and these facts indicate that the decomposition mechanisms for sapwood are the same as for heartwood. The experimental values of the activation energies in this work are of the same order of magnitude as in the references.

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